cule. The corresponding undeuterated substance (prepared in the same way) was a new compound.

Anal. Calcd. for $C_{11}H_{18}NBr$: C, 54.10; H, 7.43. Found: C, 54.21; H, 7.78.

Kinetic Measurements.—Anhydrous ethanol was prepared by the method of Smith as modified by Manske.[23] The *t*-butyl alcohol (Eastman Kodak Co. white label) was treated with potassium and distilled. Both alcohols were shown to contain less than 0.05% water by the method of Henle.[24] Standard aqueous solutions of acid and base were prepared in the usual manner. Solutions of alkoxides were prepared by dissolving the appropriate metal in the alcohol. They were stored in polyethylene bottles and standardized just prior to use.

Reactions were carried out in a thermostat that held within 0.05° of the stated temperature. The thermometer was calibrated at the boiling and freezing points of water and at 32.38° (transition temperature of sodium sulfate decahydrate). The procedures and apparatus were essentially as described by Saunders and Williams.[4]

Styrene analyses were performed spectrophotometrically as previously described.[4] Results were usually reproducible to within 1%. With 2-phenylethyl tosylate allowance was made for the ultraviolet absorption of the predominating substitution product. The kinetics of elimination from 2-phenylethyltrimethylammonium bromide was followed by analysis for styrene, since the trimethylamine generated in the reaction precludes titrimetric analysis.

Deuterium analyses were performed by the "falling drop" method. The procedure and apparatus were essentially as described by previous workers.[25] Duplicate determinations usually agreed to within 1%.

Deuterium Exchange Study on 2-Phenylethyldimethylsulfonium-2,2-d_2 Bromide.—An ethanol solution 0.0492 *M* in sulfonium salt and 0.0983 *M* in sodium ethoxide was placed in a thermostat at 30.00° just as in the kinetic runs. Aliquots were withdrawn, quenched in 0.1001 *N* hydrochloric acid and reduced to dryness *in vacuo* with a rotary evaporator. The residues were washed with ether and analyzed for deuterium. The results were (% reaction, atoms D/molecule): 0%, 1.96; 35.9%, 1.98; 44.2%, 1.94; 62.2%, 1.94.

Reinvestigation of Kinetic Measurements on the Acetyl-substituted Sulfonium Salts.—Experimental procedures were as outlined under "Kinetic Measurements." In ethanol with the *p*-acetylsulfonium salt plots of log $[b(a - x)/a(b - x)]$ *vs.* time gave negative time intercepts. The actual concentrations at $t = 0$ were evaluated from these plots and used in recalculation of the rate constants. That solvolysis of the *p*-acetylsulfonium salt did occur was confirmed in semi-quantitative experiments. When a 0.05 *M* solution of the sulfonium salt in ethanol was allowed to stand at room temperature, spectrophotometric analysis revealed 4% styrene in 20 min. and 8% styrene in 60 min. In contrast, a solution of the sulfonium salt in water at 50° showed no detectable solvolysis in 60 min. Since an unexplained conflict with earlier work existed for the *p*-acetylsulfonium salt in water, these results were checked independently by two workers (D. H. E. and Dr. R. Glaser). They agreed with each other within experimental error.

Acetylation of Methyl 2-Phenylethyl Sulfide.—The general procedure of Foreman and McElvain[26] was followed as before.[4] With two moles of aluminum chloride per mole of sulfide the monoacetyl sulfide was obtained in 28% overall yield, or 79% based on unrecovered starting material. This sulfide gave a single sulfonium salt in 80% yield, m.p. 121° dec. (lit.[1] m.p. 121–121.5° dec.). Oxidation of the sulfonium salt with potassium permanganate[27] gave 91% of terephthalic acid which had an infrared spectrum (potassium bromide pellet) identical with that of an authentic sample.

With three moles of aluminum chloride per mole of sulfide, a monoacetyl sulfide was obtained in 67% yield. This gave a single sulfonium salt in 86% yield, m.p. 115–116° dec.

Anal. Calcd. for $C_{12}H_{17}BrOS$: C, 49.82; H, 5.92. Found: C, 50.18; H, 5.93.

Oxidation with potassium permanganate gave 72% of phthalic acid, identified by melting point and infrared spectrum.

Melting points of some mixtures of the *o*- and *p*-acetyl sulfonium salts were (% *para*, melting range in °C.): 100, 121–122°; 90, 97–112°; 50, 95–101°; 15, 100–105°; 0, 114–115°. Other mixtures not quoted followed the same general pattern, the melting range remaining about the same from 25–75% *para*. Obviously neither isomer could contain an appreciable proportion of the other without a noticeable effect on the melting point. Each sulfonium salt behaved satisfactorily in the kinetic studies (Table IV).

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[23] R. H. Manske, THIS JOURNAL, **53**, 1104 (1931); E. L. Smith, *J. Chem. Soc.*, 1288 (1927).

[24] F. Henle, *Ber.*, **53**, 719 (1920).

[25] W. von E. Doering and A. K. Hoffman, THIS JOURNAL, **77**, 521 (1955); A. S. Keston, D. Rittenberg and R. Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1937).

[26] E. L. Foreman and S. M. McElvain, THIS JOURNAL, **62**, 1435 (1940).

[27] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 198.

ROCHESTER 20, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. XXI. The Alkaline Dehydrochlorination of *meso*- and *dl*-Stilbene Dichlorides[1]

BY STANLEY J. CRISTOL AND ROBERT S. BLY, JR.

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The dehydrochlorinations of *meso*- and *dl*-stilbene dichlorides with sodium hydroxide in 92.6 wt. % ethanol are shown to be first order in base and first order in dichloride, and to follow the normal concerted elimination mechanism. Second-order rate constants are given at 34.40, 43.90 and 53.30°. Entropies and energies of activation have been calculated. The data have been discussed in terms of recent concepts of transition states for bimolecular elimination reactions.

Introduction

Differences in the reactivity of diastereoisomers have been observed for many years.[2] Young and his co-workers[3] were the first to measure accurately the reactivity difference of a pair of diastereoisomers undergoing a concerted bimolecular elimination.[3b,d] They studied the iodide ion-initiated debromination of a series of *dl*- (Ia) and *meso*- (IIIa) alkylene dibromides.

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[1] Previous paper in series: S. J. Cristol and L. E. Rademacher, THIS JOURNAL, **81**, 1600 (1959).

[2] (a) A. Michael, *J. prakt. Chem.*, **52**, 305 (1895); (b) J. Wislicenus and F. Seeler, *Ber.*, **28**, 2693 (1895); (c) P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904); (d) P. F. Frankland, *J. Chem. Soc.*, 654 (1912).

[3] (a) R. T. Dillon, W. G. Young and H. J. Lucas, THIS JOURNAL, **52**, 1953 (1930); (b) W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, **61**, 1641 (1939); (c) S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939); (d) W. G. Young, S. J. Cristol and T. Skei, *ibid.*, **65**, 2099 (1943); (e) W. G. Young, Abstracts of the Eighth National Organic Symposium, St. Louis, Mo., December, 1939.

Ia, R,R' = alkyl
b, R,R' = CH_3 (*dl*)
c, R,R' = C_6H_5

IIa, R,R' = alkyl
b, R,R' = CH_3
c, R,R' = C_6H_5

IIIa, R,R' = alkyl
b, R,R' = CH_3 (*meso*)
c, R,R' = C_6H_5

IVa, R,R' = alkyl
b, R,R' = CH_3
c, R,R' = C_6H_5

In addition to demonstrating the *trans* nature and the second-order kinetics of this reaction, their investigation showed that the reaction leading to the *trans*-olefin IV was more facile than that which resulted in the *cis* compound II. They believed their results to be due to the greater steric crowding in the transition state leading to the *cis* isomer.[3e] These conclusions have since been confirmed by other investigators using different isomeric pairs.[4]

We were interested in determining the diastereoisomeric reactivity differences which could be observed with another elimination process, namely, the alkaline dehydrochlorination reaction. We decided to study the rates of dehydrochlorination of *meso*- Va and *dl*-stilbene dichloride (VIIa) with hydroxide ion in ordinary ethanol.

Va, R = Cl (*meso*)
b, R = CH_3 (*erythro*)

VIa, R = Cl
b, R = CH_3

VIIa, R = Cl (*dl*)
b, R = CH_3 (*threo*)

VIIIa, R = Cl
b, R = CH_3

Shortly after the completion of our work, the work of Cram, Greene and DePuy[5] on eliminations from diastereoisomeric 1-chloro-1,2-diphenylpropanes (Vb and VIIb) appeared, and we are therefore able to compare our data with theirs.

Experimental

***meso*- and *dl*-Stilbene Dichlorides.**—Dry chlorine was passed into a solution of *trans*-stilbene in chloroform which had been cooled to 0° in an ice–salt-bath. The isomers were separated by fractional recrystallization from the reaction mixture and from aqueous ethanol. The yield of the *meso*-dichloride Va, m.p. 180–185°, was 30%; of *dl*-dichloride VIIa, m.p. 87–90°, 42%.[6] Further recrystallization from aqueous ethanol raised the melting point of the *meso* isomer to 190° (lit.[7] 194.5–195.5°) and the *dl* isomer to 90° (lit.[7] 93–94°).

Study of Reaction Products and Infinity Samples.—When the *meso*- and *dl*-dichlorides were heated under reflux with ethanolic sodium hydroxide for a sufficient length of time to allow the elimination of the first mole of hydrogen chloride to reach 99% completion,[8] 1-chloro-*cis*-stilbene (VIa) was obtained in 83% yield from the *meso*-dichloride Va while 1-chloro-*trans*-stilbene (VIIIa) was isolated from the *dl*-dichloride VIIa in 60% yield. No other products were found. These products are the result of *trans* elimination reactions. Loss of the second mole of chloride ion was too slow to interfere in these studies.

Measurement of Reaction Rates and Treatment of Data.—The general experimental procedure for the rate runs has been described previously.[9] The extent of reaction was followed by Volhard titration of the liberated chloride ion. The modified procedure of Kolthoff and Sandell[10] was used and the solutions were stirred rapidly by means of a magnetic stirrer during the titrations.

The eliminations were approximately first order in base and first order in dichloride. The rates were run as pseudo-first-order systems by using a large excess of base so that a first-order rate law was followed. The pseudo-first-order rate constant, k_1, for each run was obtained from the slope of the best straight line drawn by inspection through the appropriate points on a plot of log $(1-\phi)$ *vs.* time, where ϕ represents the fraction of dichloride reacted at time t. Division of k_1 by the base concentration gave the second-order constant, k_2. These second-order rate constants are given at various temperatures and concentrations in Table I. The base used was sodium hydroxide and the solvent was ordinary (92.6 wt. %) ethanol.

TABLE I

DATA AND REACTION RATE CONSTANTS FOR DEHYDROCHLORINATION OF *dl*- AND *meso*-STILBENE DICHLORIDES WITH SODIUM HYDROXIDE IN 92.6% ETHANOL

Dichloride	Temp., °C.	Compd., mole/l.	OH^-, mole/l.	ClO_4^-, mole/l.	10^4k_2 l./sec./mole	10^4k_2, av.[a]
dl-Stilbene	34.40	0.002768	0.0881		14.5	14.5
		.002768	.1050		14.6	
	43.90	.007988	.1219		41.2	41.6
		.008945	.1233		41.9	
		.007988	.2439		36.1	
		.007988	.2439		36.2	
	53.30	.002768	.0984		95.2	90.3
		.002768	.0988		85.4	
		.008756	.2421		80.8	
		.007860	.2434		87.8	
meso-Stilbene	34.40	.002263	.0969		1.62	1.60
		.002365	.0965		1.57	
	43.90	.002454	.0495		5.38	
		.002489	.0501		5.24	
		.002421	.0471	0.0490	4.34	
		.002483	.0474	.0981	4.22	
		.002254	.0478	.1471	4.25	
		.002553	.0979		4.81	4.80
		.002564	.0977		4.79	
	53.30	.003284	.0963		16.7	
		.004992	.0968		13.9	14.9
		.003500	.0972		14.0	

[a] Averages calculated at hydroxide ion concentrations about 0.1 *M*.

In most cases the pseudo-first-order plots gave good straight lines up to 50–55% reaction for the *meso*-dichloride and 70–75% for the *dl*-isomer. Beyond this point the rate usually slowed down and the final points fell somewhat above

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[4] (a) D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 1066 (1950); D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951); G. H. Alt and D. H. R. Barton, *ibid.*, 4284 (1954); (b) J. A. Berson and R. S. Swidler, THIS JOURNAL, **76**, 4057 (1954); (c) J. Weinstock, S. N. Lewis and F. G. Bordwell, *ibid.*, **78**, 6072 (1956); (d) S. J. Cristol, J. Q. Weber and M. C. Brindell, *ibid.*, **78**, 598 (1956).

[5] D. J. Cram, F. D. Greene and C. H. DePuy, *ibid.*, **78**, 790 (1956).

[6] Care was taken not to "over-chlorinate" the solution, since this results in the formation of a viscous yellow oil which makes purification of the *dl* compound extremely difficult. The melting points must be taken on a Dennis bar to prevent isomerization. If the *dl* compound is heated slowly, it softens at 90° and finally melts at 160°. The *meso*-dichloride, when heated slowly, softens above 160°, and finally clears at about 190°.

[7] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

[8] The approximate times required were calculated from the previously determined rate constants for elimination; see Table I.

[9] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., rev. ed., 1943, p. 573.

a line drawn through the earlier points.[11] The constants were calculated from the best straight lines drawn by inspection. No attempt was made to include the points at the higher percentage reactions if they did not follow this line.

Reactions run at different base concentrations gave slightly different second-order rate constants. In each case an *increase* in the base concentration caused a *decrease* in the second-order rate constant. When the base concentration was doubled in the rates run at 43.90°, the second-order rate constant, k_2, was lowered by 10% in the case of the *dl*-compound and by 13% in the case of the *meso*-dichloride. When, in the case of the *meso* compound, enough perchlorate ion was added to the less basic solution to make the ionic strength of the reaction mixture equal to that of the more concentrated solution, the resulting second-order rate constant was decreased by 18%. Thus, it seems reasonable to consider that this observed change in the second-order rate constants with base concentration is primarily due to the effect of the ionic atmosphere rather than the failure of the reaction to obey second-order kinetics.

That the reaction is dependent upon base is shown by the fact that both diastereoisomeric dichlorides are stable in the rate solvent in the absence of base.

The activation energies were calculated from a plot of $1/T$ *vs.* log k_2 in accordance with the Arrhenius equation.[12]

The entropies of activation were calculated in the usual manner from the second-order rate constants, k_2 at 43.00°, read from the Arrhenius plot, using the Eyring equation.[13] Values of the Arrhenius energy of activation, E_{act} and the entropy of activation, ΔS^*, are shown in Table II.

TABLE II

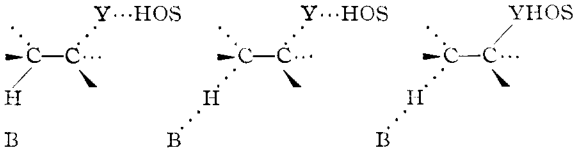
ACTIVATION ENERGIES AND ENTROPIES FOR THE DEHYDROCHLORINATION OF *dl*- AND *meso*-STILBENE DICHLORIDES

Dichloride	$10^4 k_2$, 43°, l./mole/sec.	E_{act}, kcal./mole	ΔS^*, e.u.
dl-Stilbene	36.0	19.4	−10
meso-Stilbene	4.50	23.6	− 1

Results and Discussion

It may be noted that *dl*-stilbene dichloride (VIIa) reacts with sodium hydroxide in ordinary ethanol at 43° to give 1-chloro-*trans*-stilbene (VIIIa), about 8 times faster than the *meso* diastereoisomer Va gives 1-chloro-*cis*-stilbene (VIa). The relative rate data are consistent with the idea that the transition state for the elimination process in these cases bears a marked resemblance to the products, and that the *cis*-stilbene VIa is considerably less stable than the *trans*-stilbene VIIIa because of the significantly greater steric strains (and consequent steric inhibition of resonance[14]) involved between two *cis*-phenyl groups on the one hand and a *cis*-phenyl group and a chlorine atom on the other hand.

Cram, Greene and DePuy[5] have suggested that three canonical forms IX, X and XI, where B is base and SOH the solvent, may contribute to the transition state for bimolecular elimination. They have pointed out that only if X is the major contributing form (*i.e.*, only if the transition state has considerable olefin character) will the groups attached to the carbon atoms become markedly eclipsed in the transition state. Thus only in such a situation will the relative stabilities of the olefinic products control the relative reactivities of the diastereoisomers.[15,16] They showed that the diastereoisomeric reactivity ratios could be varied by factors of as much as 80 by varying the base, the solvent or the leaving group Y in the 1,2-diphenyl-1-propyl system, and argued that high values of diastereoisomeric reactivity ratios were consistent with transition states resembling X while low values were consistent with transition states resembling either IX or XI. Similar arguments have been adduced in β-arylethyl systems.[17,18]


IX X XI

Cram and his co-workers argued that a system with a transition state related to IX would show a small difference in diastereoisomer reactivity, as the stabilities of diastereoisomers ordinarily do not differ markedly, and in fact observed at 50° a reactivity ratio for *threo*-1,2-diphenyl-1-propyl chloride (VIIb) *vs.* the *erythro* isomer Vb of only 1.1 with sodium ethoxide as base and absolute ethanol as solvent. As the products of the reaction (α-methyl-*trans*-stilbene and α-methyl-*cis*-stilbene, respectively) differ in stability by at least 2.3 kcal./mole,[5] a large reactivity ratio would be anticipated if the transition state resembled the products. This was, in fact, observed with stronger base, potassium *t*-butoxide in *t*-butyl alcohol, where the reactivity ratio at 50° was increased to 15.

Unfortunately our experiments with VIIa and Va were carried out in 92.6% ethanol with sodium hydroxide as base and are therefore not directly comparable with those of Cram. However, it is clear that our conditions (weaker base, better ionizing solvent) could lead to greater contributions from IX, and that had we used absolute ethanol and sodium ethoxide, our observed reactivity ratio of 8 would have been increased, if the Cram treatment is correct. It is of interest, then, that changing a β-methyl substituent to a β-chloro substituent in the 1,2-diphenyl-1-ethyl systems under consideration modifies the reactivity ratio so markedly. This may be rationalized in terms of the Cram treatment as it is quite reasonable to assume that (compared to methyl) the β-chlorine atom destabilizes the resonance form IX (with its carbonium-ion-like character) and destabilizes structures X and XI (where the acidity of the proton being removed is of consequence). Our data then are consistent with the ideas that the concerted elimination process may have a variation in transition state,[5] although the examples we are here reporting appear to be close to the classical type.[9,19] The markedly greater tend-

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(11) This may be due to one or several effects such as a slight impurity in the starting dichloride, the reaction of some of the base with the walls of the container, and the errors inherent in running a second-order rate as if it were pseudo-first-order.

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 23. Because of the effect of ionic strength, only rate constants determined at approximately 0.1 M base concentration were used for this calculation.

(13) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

(14) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 84.

(15) D. Y. Curtin and D. B. Kellom, THIS JOURNAL, **75**, 6011 (1953).

(16) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(17) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **79**, 3710 (1957).

(18) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

(19) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951).

ency of the chlorine-activated compounds to undergo bimolecular elimination is shown by their greater reactivities (second-order rate constants are 300-2400 times as great as the methyl analogs).

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BOULDER, COLO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

Isomers for Electrophilic Studies. Preparation of and Structural Assignments to *cis*- and *trans*-4-Methylcyclohexylmercuric Bromides[1,2,3]

BY FREDERICK R. JENSEN AND LAIRD H. GALE[4]

RECEIVED MARCH 21, 1959

cis- and *trans*-4-methylcyclohexylmercuric bromides have been prepared in pure form in order to obtain a pair of stereoisomers suitable for studying electrophilic aliphatic substitution. The configurational assignments were largely based on the observed C–D axial and equatorial infrared absorption frequencies of the 1-deuterated isomers. In connection with these results, it was found that the group containing the mercury atom, as compared to the methyl group, has a relatively small preference for equatorial over axial conformation.

Although considerable attention has been devoted to nucleophilic and homolytic aliphatic substitution, the physical–organic chemistry of electrophilic aliphatic substitution has been largely ignored. This is due to a substantial extent to the difficulty of obtaining stereoisomers of aliphatic compounds which undergo electrophilic substitution. The present paper reviews the compounds which have been used in electrophilic studies and reports the preparation of and structural assignments to a pair of simple aliphatic isomeric mercury compounds, *cis*- and *trans*-4-methylcyclohexylmercuric bromides. Organomercurials have been selected because of their high stability and because they can be readily converted to other organometallic compounds. Geometrical rather than optical isomers were chosen because of the relative ease of establishing the configuration of the compounds.

Until the recent report of the preparation of optically active *sec*-butylmercuric bromide,[5,6] no simple isomeric saturated organometallic compounds were available for electrophilic substitution studies, and the result of studies with these compounds have been only reported in preliminary form.[6] However, studies have been reported using stereochemically complex organomercurials. *cis*- and *trans*-2-methoxycyclohexylmercuric chloride have been used for stereochemical studies.[7–9] The results with these compounds are not definitive since it is possible that the neighboring methoxy group participates in the reactions and influences the stereochemistry. Also, a full analysis of these results is complicated by the conflict between the earlier assignment of structure by X-ray analysis[10] and the assignment from chemical studies.[11] Stereochemical studies have been reported utilizing the diastereomers of 3-bromomercuricamphor[12] and the *l*-methyl ester of α-bromomercuriphenylacetic acid.[13] These compounds are also unsuited for definitive stereochemical studies since they contain permanent asymmetric induction and have groups near the reaction center which contain unshared pairs of electrons.

The preliminary account of a study of electrophilic substitution utilizing simple stereoisomers not of organometallic origin has been reported.[14] In this study, the fate of the 2-phenylbutyl carbanion generated from an optically active source was investigated.

Results and Discussion

A mixture of the isomeric 4-methylcyclohexylmercuric bromides was prepared in 65% yield by treating 4-methylcyclohexylmagnesium bromide with mercuric bromide. A crude separation of the isomers was obtained based on their different solubilities in benzene. The less soluble *trans* isomer was further purified by recrystallizing from benzene yielding pure *trans*-4-methylcyclohexylmercuric bromide with a m.p. 157.7–158.0°. The crude *cis* isomer was purified by chromatography on alumina yielding pure *cis*-4-methylcyclohexylmercuric bromide with a m.p. 130.8–131.2°. To our knowledge, this is the first report of the use of chromatography to purify an organometallic compound.

The 4-methylcyclohexyl bromide (I) was obtained from the Hunsdiecker reaction on *cis*- or *trans*-4-methylcyclohexanecarboxylic acid. This synthetic route was necessary because of the difficulty in converting 4-alkylcyclohexanols to the corresponding bromides without rearrangement.[15]

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(1) Electrophilic Aliphatic Substitution III, Organomercurials, I.

(2) This work has been supported in part by a grant from the Research Corporation.

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(8) G. F. Wright, *Can. J. Chem.*, **30**, 268 (1952).

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